RECOMMENDED GUIDELINES FOR MEASURING ORGANIC COMPOUNDS IN PUGET SOUND WATER, SEDIMENT AND TISSUE SAMPLES

Prepared for

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List of ACRONYMS

AET	Apparent Effects Threshold
ANSI	American National Standards Institute
APHA	American Public Health Association
ASQC	American Society of Quality Control
BHC	Benzene Hexachloride (represents all isomers of hexachlorocyclohexane)
CCC	Calibration Check Compound
CF	Calibration Factor
CLP	Contract Laboratory Program
CFR	Code of Federal Regulations
CRDL	Contract Required Detection Limit
CRM	Certified Reference Material
CSL	Cleanup Screening Level
DAIS	Dredged Analysis Information System
DDD	2,2-Bis(4-chlorophenyl)-1,1-dichloroethane
DDE	2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene
DDT	1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane
DFTPP	Decafluorotriphenylphosphine
DQO	Data Quality Objective
ELCD	Electrolytic Conductivity Detector
EPA	United States Environmental Protection Agency
GC/ECD	Gas Chromatography/Electron Capture Detector
GC/MS	Gas Chromatography/Mass Spectrometry
HPAH	High Molecular Weight Polycyclic Aromatic Hydrocarbons
IRIS	Integrated Risk Information System
LCS	Laboratory Control Sample
LLD	Lower Limit of Detection
LPAH	Low Molecular Weight Polycyclic Aromatic Hydrocarbons
MCL	Maximum Contaminant Level
MCUL	Minimum Cleanup Level
MDL	Method Detection Limit
ML	Minimum Limit
MS	Matrix Spike
MSA	Method of Standard Addition
MSD	Matrix Spike Duplicate
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-*p*-dioxin
PCDF	Polychlorinated Dibenzofuran
PID	Photoionization Detector
PQL	Practical Quantitation Limit
PSAMP	Puget Sound Ambient Monitoring Program
PSDDA	Puget Sound Dredged Disposal Analysis
PSEP	Puget Sound Estuary Program
PSP & G	Puget Sound Protocols and Guidelines
PSWQA	Puget Sound Water Quality Authority

PSWQAT	Puget Sound Water Quality Action Team (formerly PSWQA)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RDL	Reporting Detection Limit
RF	Response Factor
RM	Reference Material
RPD	Relative Percent Difference
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SCUM1	Sediment Source Control Standards Users Manual
SCUM2	Sediment Cleanup Standards Users Manual
SDL	Sample Detection Limit
SEDQUAL	Sediment Quality Database
SIM	Selective Ion Monitoring
SMB	Spiked Method Blank
SMS	Sediment Management Standards
SOP	Standard Operating Procedure
SPCC	System Performance Check Compound
SQS	Sediment Quality Standards
SRM	Standard Reference Material
SW-846	EPA Test Methods for Evaluating Solid Waste (SW-846 3rd edition)
TCDD	2,3,7,8 Congener of Tetrachloro Dibenzo-*p*-Dioxin
TOC	Total Organic Carbon
VOA	Volatile Organic Analytes (or Analysis)
WAC	Washington Administrative Code
WDOE	Washington State Department of Ecology

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Cheryl Kamera and Dana Walker of the Metro Environmental Laboratory were the project managers. Dr. John Armstrong of the United States Environmental Protection Agency (EPA) and Dr. Timothy Ransom (PSWQAT) were the project monitors.

1. INTRODUCTION

As in previous revisions, the overall intent of the following recommendations is to advocate for a consistent approach to analyzing Puget Sound samples for organic constituents. The goal of this revision, which is intended to replace the December 1989 version, is to recommend procedures so that consistency in data collection, analysis and reporting may be attained by various researchers and resource agencies working in Puget Sound. It is hoped that this will lead to data that are comparable, of a known quality and are achievable at a reasonable cost. If this goal is achieved, most data collected in Puget Sound should be directly comparable and thereby capable of being integrated into a Sound-wide database. Such a database is necessary for developing and maintaining a comprehensive water quality management program for Puget Sound.

From surveys, workshops and phone and in person interviews conducted over the past 2 years, the original organics Puget Sound Protocols and Guidelines (PSP&Gs) have been revised to reflect the current opinions and recommendations of primary investigators who provide data for the regional databases. These guidelines were revised with the assistance of representatives from organizations that fund or conduct environmental studies in the Puget Sound region (see Table 1).

Thorough project planning is essential, due to the inherent complexity of sampling and analysis activities. The presence of multiple programs and activities in the Puget Sound region further enhances the need for project planning. This chapter should be used in conjunction with the *Recommended Guidelines for Sampling Marine Sediment, Water Column and Tissue in Puget Sound* (PSEP, 1997a) and the *Recommended Quality Assurance and Quality Control Guidelines for the Collection of Environmental Data in Puget Sound* (PSEP, 1997b).

Whenever feasible, it is recommended that the guidelines in this document be used for all Puget Sound studies. It remains the responsibility of each project manager to become familiar with program requirements and to conduct sampling and analysis accordingly.

Although the following methods are recommended for most studies conducted in Puget Sound, departures from these recommendations may be necessary to meet the special requirements of individual projects. If such departures are made, however, the funding agency or investigator should be aware that the resulting data may not be compatible with other data. In some instances, data collected using different methods have been inappropriately combined in the past. In other instances, when the methods were adequately intercalibrated, data may have been combined appropriately. The use of standardized methodologies should aid in producing data of definable quality, enhancing our ability to compare data sets.

TABLE 1
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2. GENERAL CONSIDERATIONS

2.1 Data Quality Objectives

A formal planning process, as described in Section 2 of the QA Chapter (PSEP, 1997b), is used to ensure that project data support project objectives. During this planning process, analytical methods and other related activities are specified. These decisions are based on the project data quality objectives. The selection of a specific analytical method must be driven by the intended end use of the data. After specifying the expected uses of the data, data quality objectives should be developed. Section 2.4 of the QA Chapter (PSEP, 1997b) offers guidance regarding how to develop data quality objectives for a specific project.

To best ensure that the data quality objectives for a project are met, the laboratory that will be performing the analyses must be involved in project planning well in advance of receipt of samples.

2.2 Contamination and Low Level Work

It is advisable for laboratories that perform organic analyses to conduct trace-level work on an ongoing basis. The laboratory's quality control program should contain QC samples such as method blanks, glassware blanks and equipment blanks that allow for continually updated knowledge regarding background levels in the sample processing environment. The laboratory's QC program should address the matter of assessing contamination, identifying sources and eliminating or minimizing those sources of contamination.

Every precaution should be taken to avoid contamination at each stage of sample collection, handling, storage, preparation and analysis to prevent potential positive bias. The majority of trace organic analyses performed in support of Puget Sound programs require low detection limits making contamination control an essential factor in trace organics work. These low detection limits are challenging to current instrumentation and methods.

The best way to control contamination is to completely avoid exposure by performing operations in an area known to be free from contamination. Precautions must be taken to manage equipment used during testing. Procedures should be performed by well-trained, experienced personnel who pay strict attention to the work being done. A number of relevant points regarding contamination and how to manage it follow.

Use a clean environment for processing samples. Restrict admittance to these areas, and train personnel in clean sample handling techniques. Dedicate areas to trace level work and isolate samples with high concentrations of organics to other areas. Physical sample handling should be kept to a minimum. Field equipment and labware must be carefully cleaned, and cleaning methods must be monitored and verified using QC samples. Exposure of samples to airborne dust should be minimized during sampling and analysis. Labware should be similarly isolated. Minimize the time between cleaning and use of labware. Cover glassware with aluminum foil and store in a clean dry place if it cannot be used immediately. Just prior to its use, glassware should be rinsed with the solvent to be used. Other sources for potential contamination are rubber, paper cap liners, pigment in marking pens, polyvinyl chloride, nylon,

methacrylate, Vycor® and talc. It is necessary to use only clean, powder-free gloves for all sample handling steps. The laboratory should be aware of potential contaminants in gloves used for sample processing. All procedures should be detailed in SOPs and followed rigorously. For low-level work, reagents must be ultrapure grade or equivalent and should never be returned to their stock containers once removed. Sample carry over at the instrument must be carefully monitored, and GC bake times, autosampler solvent rinses and sample injection order should be adjusted to eliminate any potential carry over.

2.3 Cleaning Methods for Glassware and Lab Equipment

All labware used during sample analysis must be free from possible contamination. Labware should be dedicated according to sample type and anticipated concentration of analytes. Poorly cleaned glassware can cause either positive or negative bias. For example, sediments generally contain higher levels of analytes than tissues. So contamination during analysis will be minimized if labware for these different sample types are kept separate. Phthalates from plastic sources such as gloves can contaminate glassware. Do not touch the insides of glassware with gloves. Use Teflon® squirt bottles to hold solvents or acids used to rinse glassware. Never clean glassware used for volatile analysis with methylene chloride or acetone, because these solvents will interfere with the analysis. Soap residue (e.g., sodium dodecyl sulfate), which results in a basic pH on the glassware surface, may cause degradation of certain analytes (e.g., Aldrin, Heptachlor and most organophosphate pesticides). Cracks in glassware could lead to the contamination or loss of an extract. It is critical for the glassware to be carefully scrutinized before setting up an analysis. Often there is only one chance to extract a sample due to sample amount or short holding times. A recommended approach to cleaning labware follows. Some equivalent method should be employed to clean and prepare labware, which should be documented by SOP.

2.3.1 Labware Wash

Collect dirty glassware, rinse thoroughly with cold tap water and place in hot water tub with detergent to soak for 5 minutes. Remove glassware from the tub and scrub all accessible parts. If a dishwasher is available, it can be used now for a final wash/rinse. If a dishwasher is not available for a final wash/rinse, rinse 3 times with tap water and 3 times with organic-free water and hang to dry. For glassware that can not be scrubbed, place in 5% nitric acid tub for 8 hours or overnight then rinse 3 times with tap water and 3 times with organic-free water and hang to dry. It may be necessary to use additional measures for severely dirty glassware. Carefully inspect for cracks, soap residue (hazy or cloudy surface) or dirt. It is critical that the glassware be very clean to prevent interferences during extraction. Etched glassware or glassware that will not come visually clean should be removed from trace work. Additionally, glassware may be fired in a muffle furnace or kiln (examples of temperature and times that are in use are 430^{o}C for at least 30 minutes or 350^{o}C for 4 hours) after the final wash to further clean the glassware; however, if volumetric glassware are fired, they should no longer be considered to be class A. Highly contaminated glassware may need to be fired for a longer time. Also, some chlorinated pesticides and PCBs only partially break down at these temperatures and so the glassware should be thoroughly washed if these classes of compounds have been in contact with the glassware.

2.3.2 Preparing Labware for Use

If the labware is still wet, air dry or rinse three times with high purity acetone. Just before use, rinse three times with methylene chloride; make sure the solvent touches all inside areas of glassware. Pay special attention to thin glass tubing and ground glass joints. The methylene chloride should be collected in an appropriate container for recycling or proper disposal. Labware should then be assembled and used as soon as possible.

2.4 Interferences

Interferences are generally minimized through the use of either sample cleanup steps or more selective detection systems. Changes in extraction technique may also reduce interference. Marine samples may provide a significant challenge to laboratories analyzing for trace organics because of analytical interferences. Marine sediment and tissue samples may contain high concentrations of organic materials that coextract with the analytes of interest. Even after exhaustive cleanup, many interferences may still be present. For example, sulfur will interfere with the analysis of pesticides and PCBs. Some instrumental methods are more affected by interferences than others; for example, the electron-capture detector is subject to electrophilic interferences. Certain target analytes may become interferences; for example, PCBs at high concentration can interfere with the determination of pesticides in the same sample. Also, several analytes are commonly found or used in the laboratory that may result in interferences. The extraction solvents methylene chloride and acetone interfere with volatiles analysis and bis(2-ethyl hexyl) phthalate interferes with semivolatile analysis. Another type of interference that is frequently encountered for organic analysis of marine sediments is specific to the matrix. Certain types of organic materials (such as sawdust) can result in a significant loss of spiked chemicals (such as surrogates) due to the adsorption onto the surface of the material. A similar effect occurs for very fine particulate matrices like clay. These interferences cannot be controlled through the use of clean environments or additional cleanups. The end result is usually a significant elevation of achieved detection limits, unless alternative analytical techniques or extraction procedures are used. The choice of analytical method must consider known and potential interferences. Specific information on how to minimize interferences from marine samples is found in sections of this chapter that cover the determinative techniques.

3. SAFETY CONSIDERATIONS

The laboratory must operate an active safety program. Implementation of new methods must consider the hazards of those methods. Extracts should be handled carefully due to the possible concentration of pollutants that may result from sample preparation. Even ambient monitoring samples may contain notable concentrations of pollutants. Health and safety issues need to be considered when choosing methods of analysis. Each organization participating in a project should ensure that their activities do not increase the risk to humans or the environment. When more than one method option exists, the method with fewer hazardous reagents, dangerous procedural steps or toxic by-products should be chosen. Lab workers must be trained in safe lab techniques. Appropriate engineering controls and personal protective equipment must be available and used during sample extraction, because many of the solvents used are flammable, toxic or carcinogenic. Glasswash cleaning areas should have sufficient air handling systems to allow for safe operation during all phases of glassware cleaning. During cleaning of labware, care must be taken while using acid baths. Acid or acid fumes can cause burns to skin and eyes, thus concentrations of acids and should be kept as low as feasible for decontaminating labware and sampling equipment.

4. SAMPLE ACCEPTANCE AND STORAGE CRITERIA

All samples must be collected and handled following a sampling plan that addresses the considerations discussed in Section 7, Sample Handling, of the Field Chapter (PSEP, 1996a). All sample containers should be prewashed according to the methods described in Section 2.5.2 of the Field Chapter. Alternatively, containers may be purchased precleaned. All samples must be preserved and stored according to applicable EPA approved procedures as described in the Field Chapter (PSEP, 1996a), and analysis must start prior to expiration of holding time.

When samples are received by the laboratory, adherence to the sample acceptance requirements specified in the project planning document should be verified to ensure sample integrity. The following should be considered:

- Technical validity -- sample preservation and storage are appropriate for the stability of the analyte.
- Chain of custody -- the personnel handling the sample are properly trained and authorized to do so; tampering with the sample is precluded and all sample handling is documented.

In addition, the following items should be verified: sample identification (between the sample container and the field sheet); sample bottles; and sample receipt within holding time. When applicable, any safety hazards associated with the samples should be noted, documented, and the appropriate personnel should be notified.

Tables 2, 3 and 4 of the Field Chapter (PSEP, 1996a) summarize the appropriate sample containers, sample sizes, preservation techniques, storage conditions and holding times for organic analyses. Any samples that are incorrectly preserved or not analyzed within holding times should be discussed in the narrative portion of the laboratory report, and data may need to be qualified.

Water samples should be stored in the dark at 4^{o}C until ready for extraction. In general, samples should be extracted within seven days. VOA samples should be analyzed within seven (7) days, unpreserved. For preserved VOA samples, follow holding time requirements listed in SW-846, Chapter 4. Extracts should be analyzed within 40 days from the date of extraction.

Sediment samples should be stored in the dark at 4^{o}C, on ice, or frozen at -18^{o}C (except for samples intended for volatiles analysis) until extraction. Extracts should be analyzed within 40 days. Analyses for volatile compounds should be performed within 14 days of collection, as recommended in SW-846. Samples to be analyzed for semivolatile organic compounds should be frozen if the analysis will not be performed within the recommended 14-day holding time for fresh samples. Care must be taken with frozen samples to prevent container breakage by leaving headspace for the interstitial water to expand and by freezing containers at an angle rather than in an upright position. Currently observed holding times for Puget Sound programs were established at the third annual review meeting (ARM). It is recommended that holding time be as short as possible since the stabilities of some compounds are unknown.

Information available from stability investigations provides some guidance. For sediment samples held at -18^{o}C, workshop participants discussed a general guideline of 1 year. In an unpublished study at the University of Washington School of Oceanography, replicate samples of sediment homogenates were frozen for up to 5 years and were analyzed for hydrocarbons. No significant differences in hydrocarbon concentrations were found over time. Reproducible results have been reported by the Northwest National Marine Fisheries Service (Northwest NMFS) laboratory for hydrocarbons and PCB mixtures in frozen sediment homogenates of Duwamish River reference sediments analyzed over a period of

approximately 2-3 years. Storage results over a several year period are not available for other compound classes, such as acid- or base-extractable organic compounds; hence, long-term storage of samples (i.e., >1 year) for broad-scan analyses should be undertaken with caution.

Recommended holding times for frozen tissue samples have not been established by EPA, but a 1-year maximum holding time (similar to the sediment holding time) is recommended for Puget Sound studies. Extracts should be analyzed within 40 days. Extended sample storage in a glass jar can minimize desiccation. NIST is testing the effects of long-term storage of tissues at temperatures of liquid nitrogen (-120 to -190^{o}C). At a minimum, the samples should be kept frozen at -18^{o}C until extraction. This temperature will slow biological decomposition of the sample and decrease loss of moisture. Because of the potential rupture of tissue cells upon freezing, liquid associated with the sample when thawed must be maintained as part of the sample or extracted separately and combined with the tissue extract.

5. METHODS OF ANALYSIS

5.1 Method Selection

The appendices to the QA Chapter (PSEP, 1997b) contain the relevant information necessary for a project manager to select an analytical method in conjunction with the laboratory. These appendices contain program specific limits. Additional program information is also included. It is a general recommendation that methods based on the most recent update of SW-846 (EPA 1995), *Test Methods for Evaluating Solid Waste, Third Edition* be followed whenever possible. SW-846 is a methods manual that is a "living" document. As new data and advances in analytical techniques occur, they are incorporated into the manual as new or revised methods. Although some of the broad-scan methods, such as Method 8270 for semivolatile organics, have cited method quantification limits that are too high for use in low-level analyses, the methods are flexible enough to allow for modifications that will make them appropriate for use for low-level analyses. The Washington State Department of Ecology, Quality Assurance Section also accredits laboratories for these methods. Note that throughout these guidelines, an SW-846 method reference refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

5.2 Method Performance

5.2.1 Precision and Bias

Precision is an indication of the agreement among the results of replicate measurements. The replicate samples should contain concentrations of analyte above the detection limit and they may involve the use of matrix spikes when levels of native analytes are below the detection limit. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV):

$$RSD = CV = 100 s_x / \bar{x}$$

where $\bar{x}$ is the arithmetic mean of the x_i measurements and s_x is the standard deviation.

For estimating precision between duplicate analyses the Relative Percent Difference (RPD) is used:

$$RPD = 100 \frac{|x_1 - x_2|}{(x_1 + x_2) / 2}$$

The standard deviation can be calculated as follows:

$$S_x = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]}$$

where *n* is the number of measurements.

Bias is described as the deviation due to a systematic error (i.e., a consistent tendency for results to be either greater or smaller than the true value), such as calibration error, matrix interference, inability to measure all forms of the analyte, analyte contamination, etc. The deviation due to matrix effects is assessed by comparing a measured value to an accepted reference value in a sample of known concentration (such as a standard reference material) or by determining the recovery of a known amount of analyte spiked into a sample (matrix spike). The bias due to matrix effects based on a matrix spike is indicated as:

Bias = $(X_s - X_u) - K$,

where X_s is the measured value for the spiked sample, X_u is the measured value for the unspiked sample and K is the known (calculated) spike amount. Blanks can also be useful indicators for estimating bias due to contamination. More information can be found in Section 5.7, Analytical QC.

The percent recovery (%*R*) for check standard or matrix spikes is given by:

$\%R = 100(R_s/R_t)$

where R_s is the result for the check standard or the difference between the results for the spiked and the unspiked samples and R_t is the known value for the check standard or the amount of the analyte added to the matrix spike.

Accuracy is described as the closeness of agreement between an observed value and a true or accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random (precision) component and of a systematic error (bias) component. In general, precision and bias are performance characteristics of the method as used by a particular laboratory and analyst.

5.2.2 Determining, Defining and Verifying Detection Limits

The use of detection and quantification limits is discussed in the following sections on analytical methods, QA/QC procedures and reporting requirements. To provide an appropriate context for these discussions, the definition of these terms is provided in this introductory section. Discussion of detection limits was wide ranging at the work groups on organic compound analyses. At a minimum, two types of "limits" were found to be necessary. First, a need was expressed to provide qualitative estimates of low-level responses that are detected at the maximum sensitivity of a method and instrument. This need was addressed by defining a detection limit. Second, a need was expressed to identify a level above which there is high technical confidence in the quantified result (i.e., low probability of either a false positive or false negative result at the limit). This need was satisfied by defining a quantification limit. Because of the varying definitions being used within EPA to define detection limits, we will keep our discussion at a more generic level.

The following definitions of limits are recommended for low-level analyses:

Determinations of the detection limit should be made for a minimum of four replicate analyses to provide statistical data to estimate the uncertainty of the measurement. The detection limit is estimated by multiplying the standard deviation of the standard solution or spiked sample responses by the appropriate value of the *t*-statistic for the number of replicate measurements and the desired level of confidence. For example, at the 99% confidence level, the values of Student's *t*-statistic are 4.54 for four measurements and 3.14 for seven measurements. This is analogous to the method detection limit (MDL) described in 40 CFR 136. Note that MDL actually establishes a value that will not provide falsely positive data. There is no guarantee regarding the chance of reporting a false negative at the MDL.

The following practical guidelines should be followed when determining detection limits:

The detection limit can be estimated based on the standard deviation of low-level matrix spike responses. Best professional judgment is used to adjust the detection limit upward in cases where high instrument precision (i.e., low variability) results in a calculated detection limit and equivalent instrument response less than the absolute sensitivity of the analytical instrument. As a guideline, the detection limit may be adjusted upward to reduce false negatives, but results cannot be reported for values less than the detection limit. When conducting full-scan GC/MS analyses, the determination of the detection limit requires that full spectral confirmation be met as defined by Method 8270 for semivolatiles and Method 8260 for volatiles (EPA, 1995).

The quantification limit is the minimum concentration of an analyte required to be measured and allowed to be reported without qualification as an estimated quantity for samples without substantial interferences. The quantification limit is generally based on a value that is between 5-10 times that of the detection limit, considering the amount of sample typically analyzed and the final extract volume of that method. The quantification limit must be greater than the detection limit. It is suggested that the laboratory analyze an instrument standard at or near the quantification limit to verify the quantification limit of the instrument for each compound on a periodic basis. A spiked method blank, fortified with analytes at or near the quantification limit, is also suggested to be analyzed on a periodic basis to verify the quantification limit of the method. The laboratory may use these data to generate performance based control criteria. Further guidance on generating control criteria may be found in EPA (1979) or Section 9.3.3 in the QC section of EPA methods written in the EMMC format (EPA, 1993). These control limits may be requested by project managers for inclusion in project planning documents. Certain projects may require verification of regulatory action limits, and this should be addressed in the project planning document.

At a minimum, laboratory statements of work that reference PSP&Gs for low-level analyses must specify the quantification limit as the maximum acceptable detection limit to be reported for samples without significant interferences. Reporting requirements for detection limit and quantification limit are summarized in the Data Reporting Requirements section. The detection limit and quantification limit are recommended for use as follows:

- No concentrations should be reported below the detection limit documented for a project.
- Concentrations reported between the detection limit and the quantification limit are usable after qualification (see Appendix A in the QA Chapter (PSEP, 1996b) for data qualifier definitions) as estimates below the quantification limit.
- Concentrations reported above the quantification limit are usable without qualification unless qualification is deemed appropriate during QA review.

5.3 Sample Preparation

Sample preparation for organic analyses generally involves extraction from the sample matrix followed by isolation and concentration of target analytes prior to instrumental analysis. SOPs should be followed and all deviations noted. Problems and unusual observations during preparation must be documented. The laboratory is required to record detailed notes during sample preparation and analysis to help trace problems or analytical anomalies. Information regarding sample collection, preservation, amounts and holding times can be found in Tables 2, 3 and 4 in the Field Chapter (PSEP, 1997a). Recommendations for sample preparation are presented by matrix in the following sections.

5.3.1 Marine Water

At present, there are no EPA approved methods intended specifically for saline water, although widely accepted methods have existed for some time (e.g., Strickland and Parsons, 1972; Grasshoff et al., 1983; and Parsons et al., 1984). In general, it is recommended that methods from EPA (1995) be followed, using the most recent approved edition. Marine water matrix is not listed specifically in the SW-846 methods; however, this matrix is amenable to these methods.

In general, the entire sample should be used for the analysis followed by at least two (2) solvent rinses of the sample container, which should then be combined with the extracting solvent. The sample container must be solvent rinsed because many target analytes adhere strongly to glass.

In general, the organic content of matter in marine water can be divided into two categories: dissolved and particulate. Particulate matter includes material having a diameter greater than 0.45 µm, whereas the dissolved category includes true dissolved matter and colloidal material that passes through a 0.45-µm membrane filter. The determination of total concentrations (i.e., particulate plus dissolved) of individual compounds is relatively straight forward with regard to matrix interferences. However, because the concentration of any individual compound, total or dissolved, will rarely exceed 10 µg/L (Riley and Chester, 1971), detection can be quite difficult. It is normally necessary to concentrate many liters of sample to obtain sufficient concentrations for analysis. The problem is exacerbated if concentrations of particulate analytes are to be determined.

It is important to work with the laboratory and sampling team to determine the best approach for the analysis of marine waters. Most analyses conducted in support of the major Puget Sound programs to date for analysis of saline waters have followed SW-846 Method 3520, *Continuous Liquid-Liquid Extraction*. Method 3510, *Separatory Funnel Extraction*, is an acceptable alternative, although analyte recoveries may not be as complete compared to Method 3520. Modifications to these methods may be necessary to achieve low-level detection limits, such as reducing the suggested final volumes cited by the method or possibly increasing the sample size.

5.3.2 Sediment

It is extremely important that the sample be clearly defined prior to starting the analysis. In general, current references recommend that excess or overlaying water in a sample be decanted prior to subsampling (EPA, 1987; EPA, 1994; EPA, 1995). For some projects, the concentration of analytes in the interstitial water associated with the solid phase may be of interest (e.g., oiled sediments). Decanting, centrifugation and discarding this water may bias the results. If concentrations in the whole sample (i.e., including interstitial water) are of interest, the decanted water should be extracted as a liquid sample and the resulting extract combined with the sediment extract (EPA, 1987). Alternatively, the overlaying water in the sample can be mixed into the sediment prior to subsampling. The desired procedure should be specified in the project planning document to ensure the generation of data appropriate to project goals. If samples are decanted, this should be reported with the final data and the percent solids should be determined on a decanted sample.

Most analyses of marine sediments conducted to date in support of the major Puget Sound programs (see the QA Chapter, PSEP 1997b, Section 1) have followed SW-846. Method 3540, *Soxhlet Extraction*, is the recommended extraction procedure for marine sediments. Method 3550, *Sonication Extraction*, is an acceptable alternative; however, the laboratory must confirm that recoveries are equivalent to Method 3540. Modifications to these methods may be necessary to achieve low-level detection limits, such as reducing the suggested final volumes cited by the method and/or starting with larger sample sizes. All sediment samples being analyzed for semivolatile organics must be subjected to Method 3640, *Gel-Permeation Chromatography* (GPC). Alumina or Florisil cleanups (Methods 3610 and 3620, respectively) should be performed for analyses of pesticides and PCBs. For PCBs alone, a strong acid/oxidizer cleanup of the final extract can be employed using Method 3565. Pesticide analysis may also require that sulfur be removed from the sample extract prior to GC/ECD analysis. This can be done using Method 3660, *Sulfur Cleanup*.

Preparation of elutriates should follow the U.S. Army Corps of Engineers' Dredge Material Test Manual (EPA, 1994).

5.3.3 Tissue

Low-level analyses should have quantification limits of 20-100 µg/kg (wet weight) for acid/base/neutral compounds, 0.1-2 µg/kg (wet weight) for most pesticides, and 1-5 µg/kg (wet weight) for PCBs. Tissue extracts contain high concentrations of lipids and require a reduction in the levels of biological macromolecules by GPC or HPLC prior to analysis.

Tissue samples must be homogenized prior to extraction to ensure that aliquots for analysis are representative of the organism and to improve extraction efficiency. If samples are to be analyzed for other parameters, in addition to organics, consider the contamination issues for sample handling of all parameters during the homogenization step. Thaw frozen samples immediately before homogenizing. When homogenizing the samples, include any liquid that is present with the sample. Minimize the sample handling during this step to reduce the risk of contamination. When possible, homogenize the sample in the sampling container. Tissue grinders or homogenizers (see below) are commercially available. For organic analysis, choose a grinder with blades made of titanium, tantalum or high quality stainless steel. A Waring type blender with stainless steel blades and an glass jar can be used. A rinsate blank should be collected from the homogenization apparatus to verify that decontamination procedures are sufficient. The sample should be homogenized to a paste-like consistency. Larger samples may be cut into 2.5 cm cubes with titanium or high quality stainless steel knives before grinding. No chunks should remain in the sample because these may not be extracted or digested efficiently. Homogenized samples must be stored frozen, thawing only for analysis.

There are times when the amount of sample available may be severely limited, such as with organ tissue. If this is the case, it is particularly important to conserve sample during the homogenization step. Choose a grinder that is designed for small sample sizes and homogenize the sample in the original sample container to avoid losing sample in the process of transferring sample from one container to another. In addition, it may be necessary for the project manager to assign priority of analyses when sample size is limited.

Generally, a laboratory sample of approximately 30 grams (wet weight) is adequate to attain the recommended detection limit and quantification limit for full-scan GC/MS analyses using standard instrumentation. Sensitivity can be improved by decreasing the final extract volume from 1.0 to 0.5 mL and increasing the GC/MS injection volume from 1 to 2 µL. A smaller sample size (e.g., 3 grams) may be adequate if the instrument sensitivity (including alternatives to GC/MS, such as analysis of chlorinated benzenes by GC/ECD) or extract volume can be adjusted appropriately. Small sample sizes may adversely affect the detection limits that can be attained; conversely, large sample sizes may result in interferences from lipid materials that must be removed. The analyst should be cautioned that by increasing sample size and/or injection volumes and concentrating sample extracts will enhance analytical interferences in approximately the same proportion. Collection of at least 100 grams (wet weight) is recommended for samples that must be analyzed in duplicate. Note that tissue detection limits in this document (referenced above) are listed on a wet-weight rather than dry-weight basis.

Some laboratories preprepare the samples prior to extraction by grinding and homogenization (e.g., with a Tekmar Tissumizer® or a Waring type blender) with sodium sulfate to dry the tissue samples. It also helps macerate the tissue and helps produce a paste that is readily extracted. Cleaned sand can also be used for maceration. If tissues are dried with sodium sulfate without solvent present, extreme care must be exercised to avoid loss of analytes from volatilization (e.g., analytes as volatile or more volatile than phenanthrene). Other laboratories (e.g., EPA Manchester) combine the grinding and homogenization with the extraction and do not dry the tissue.

Once a sample has been homogenized and dried with sodium sulfate, Method 3540, *Sohxlet Extraction*, or Method 3550, *Sonication Extraction*, can be used for extraction. For Method 3550, it is recommended that an icebath be used to prevent sample heating and a possible subsequent loss of the more volatile analytes. As previously mentioned, Method 3660, *Gel-Permeation Chromatography*, must be used to cleanup tissue extracts. It can be helpful to take the extract immediately prior to GPC and cap and freeze it at 4°C overnight, then filter. This allows excess lipids to drop out of solution, reducing the risk of GPC clogging. Note that it is not recommended to use any of the strong acid cleanups for tissue extracts due to emulsion formation. It is highly recommended to use Florosil or Alumina to clean up adipose tissue extracts, in addition to GPC, when analyzing for pesticides.

5.4 Instrumental Analysis

Each of the methods listed in Table 2 has specific QA/QC requirements. In some cases the method also includes a required cleanup or sample preparation (e.g., Method 8290). At a June 1995 workshop of laboratories, it was agreed that regardless of the matrix for a particular sample, once it has been extracted, cleaned up and concentrated, the determinative method would remain the same. A specific method should be outlined in the project planning document. There should be adequate dialogue with the laboratory to ensure method selection to best meet the detection limit and QC requirements for the project. This should include a discussion of the tradeoffs between lower detection limits and selectivity among the various methods, especially for those compounds addressed by more than one method.

TABLE 2
RECOMMENDED DETERMINATIVE METHODS

SW-846 Determinative Methods[1]	Analytes
8021	Volatile Organics by GC ELCD/PID
8040[a]	Chlorinated phenols by GC/ECD
8061	Phthalate esters by GC/ECD
8081	Organochlorine pesticides and PCBs
8121	Chlorinated hydrocarbons by GC/ECD
8151	Chlorinated acid herbicides by GC/ECD
8260	Volatile organics by capillary GC/MS
8270	Semivolatile organics by capillary GC/MS
8290	Dioxins by high resolution GC/MS
9060[b]	Total Organic Carbon
Additional non-SW-846 Methods	
EPA 1613	Dioxins by high resolution GC/MS
EPA 1625[c]	Semivolatile organics by isotope dilution
EPA 1653	Chlorinated phenols, Guaiacols and Catechols
EPA 1668 Draft	Coplanar PCBs by high resolution GC/MS
Organics Chapter PSEP 1996	Organotins
Standard Method 5310B[b]	Total Organic Carbon

Notes:

1. Note that throughout these guidelines, an SW-846 method reference refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

a. Note that only the section of 8041 addressing the derivatization of the chlorophenols and the subsequent analysis by GC/ECD is appropriate for use on low-level marine samples.

b. See Appendix D for specific modifications that are required to use these methods.

c. Method 1625 is not currently being requested for most of the major programs in Puget Sound on a routine basis. Few laboratories are currently capable of performing the test due to the high cost of materials associated with this analysis. It is recommended that Method 1625 only be used for projects where previous samples have been analyzed by that method.

Because certain programs (e.g., SMS) require final results that are normalized to sample TOC concentrations, meeting the program detection limits can be a challenge. WDOE has issued several guidance papers or Technical Information Memorandums (e.g., Michelsen, 1992) regarding organic carbon normalization of sediment data. The memorandum is presented as Appendix D of this chapter to provide additional clarification and guidance.

Laboratories have been forced to either employ the more sensitive, but less specific, GC analyses (e.g., Method 8121 for the dichlorobenzenes) or use a GC/MS technique known as selective ion monitoring (SIM). Currently there is very little EPA guidance on using GC/MS SIM as a determinative technique. Appendix B presents a recommended approach for SIM, and Appendix A shows the currently recommended method for organotins.

5.5 Additional Techniques

There are several new techniques that should be mentioned. These have only been employed on a relatively small number of projects in the Puget Sound; however, Method 4000, *Immunoassay Analysis,* and Method 3535, *Solid Phase Extraction (SPE),* offer options to help reduce solvent usage and costs for the analysis of aqueous samples. These alternate approaches may also help to reduce detection limits. When using these methods consider and account for data needs, noting whether dissolved or particulate data are needed. For sediments, Method 3545, *Accelerated Solvent Extraction* has shown promise to maintain or improve on extraction efficiencies, while greatly reducing solvent volumes and extraction times.

5.6 Calibration

The procedure used for calibration of analytical instruments affects the accuracy of analytical results. Calibration, in this section, refers to determination of the response of the instrument across a range of concentrations for each analyte of interest (initial calibration). Additionally, continuing calibration verification, action limits and corrective action are discussed. A distinction should be made between an internal standard versus an external standard with regards to definitions of factors. In an internal standard technique the use of the term RF or response factor is used--the CLP will use the term RRF for relative response factor. For an external standard technique the term CF or calibration factor is used.

For GC/MS, the instrument must pass mass spectrometer tuning criteria prior to analysis of any standards. The tuning criteria can be found in the specific GC/MS methods in SW-846.

For GC analyses of pesticides a column degradation check using endrin and DDT should be performed prior to analysis of standards. The specific performance criteria can be found in Method 8081.

In general, follow the calibration requirements set forth in the specific SW-846 method that will be used. Special calibration requirements of projects requiring low-level analyses should be addressed in the project planning document after consultation with the laboratory.

5.6.1 Initial Calibration

Both external standard calibration and internal standard calibration procedures are used for organic analyses. External standard calibration involves the analysis of standard solutions, independent of the samples, to determine the relationship between instrument response and concentration for the substance being measured. Internal standard calibration is a procedure in which the instrument response from each analyte is determined relative to the responses from one or more internal standards added to every standard. An ideal internal standard is a compound with chemical and physical properties similar to those of the analyte, but is not likely to be found in the sample. The internal standard method of calibration is recommended, when available. Internal standards are specified in the analytical methods.

5.6.1.1 Frequency

Equipment should undergo initial calibration at the beginning of the project before any samples are analyzed, after each major equipment disruption, and any time continuing calibration does not meet criteria. RF or CF values must be determined for at least five concentration levels. The standard concentrations tested should encompass the range of expected sample concentrations. The lowest standard in this curve should be analyzed at an on-column concentration equivalent to the quantification limit for the sample set. Note that SW-846 allows for the construction of calibration curves other than an average response type. Refer to the specific SW-846 method or Method 8000 for guidance.

5.6.1.2 Action Limit

Refer to the specific SW-846 method for a detailed discussion of requirements. For most compounds, action limits are based on the variation among the RFs or CFs calculated during the initial calibration. The percent relative standard deviation (RSD) obtained from the RF in the initial calibration will have specific limits as stated in the method being followed. In general, internal standard methods have a 30% RSD requirement and external methods have a 20% RSD requirement. However, for the GC/MS methods the general RSD criteria is 15% to show sufficient linearity to employ an average response factor, if the RSD of any compound is greater than 15%, see Section 7 in Method 8000 for options on dealing with other calibration approaches. Note that certain compounds (i.e., the Calibration Check Compounds or CCCs and the System Performance Check Compounds or SPCCs) have specific performance requirements that must be met, otherwise the curve will be rejected. If other than an average response is used for calibration, refer to the specific SW-846 method or Method 8000 for guidance.

5.6.1.3 Corrective Action

Failure to meet calibration requirements before analysis of samples may be cause for data qualification or even omitting the data from regional databases. Note that in a multianalyte method, failure to meet the calibration requirement for a small percentage of analytes should not be cause to omit the entire analysis for a sample from the database. Omission should be determined on an analyte by analyte basis.

Initial calibration results within acceptable limits must be verified prior to the analysis of samples. Summary data documenting initial calibration and any episodes requiring recalibration and the corresponding recalibration data should be maintained with the analytical results (see Section 6).

5.6.2 Continuing Calibration Verification

Ongoing single-point calibration verification is used to check that the original calibration curve continues to be valid. It is acceptable to use the continuing calibration verification standard to quantify subsequent analyses when a response factor is used; however, consideration should be made as to possible quantatation bias created by this approach. On the other hand, calibrating with the ongoing single-point calibration verification allows for daily instrument variation to be taken into consideration.

5.6.2.1 Frequency

For GC/MS analyses, calibration should be checked at the beginning of each analytical instrument sequence , and at least once every 12 hours of analysis.

For GC/ECD analyses, calibration should be checked at the beginning of each analytical instrument sequence, every 12 hours (or every 10 samples, whichever is less frequent) and after the last sample of each analytical instrument sequence.

For internal standard analyses, all area counts for the internal standard in each sample analysis should be compared to the internal standard area counts in the ongoing calibration verification check standard.

For additional guidance regarding continuing calibration verification, refer to the specific SW-846 method or Method 8000.

On a periodic basis, a standard should be analyzed at or near the quantification limit to verify the instrument's performance. Specific criteria may be developed by the laboratory to indicate if the instrument is in control. Additional requirements may be outlined in the project planning document, but should be done after substantial discussion with the laboratory.

5.6.2.2 Action Limit

The continuing calibration RF or CF determined for specific compounds should meet the following action limits: 1) the CF determined for PCB and pesticides analyzed with GC/ECD should be within 15% of the initial calibration CF; 2) those semivolatile and volatile compounds (CCCs) that must meet the ongoing calibration 20% control limits can be found in Methods 8270 and 8260; and 3) the endrin/DDT column degradation check should be less than 20% for either endrin or DDT and the total must be less than 30%. For more guidance regarding continuing calibration verification action limits, refer to the specific SW-846 method or Method 8000.

5.6.2.3 Corrective Action

If the action limit is not met, the initial calibration will have to be repeated. Samples analyzed after a continuing calibration verification that has not met action limits should be reanalyzed under acceptable conditions. For more guidance regarding continuing calibration verification corrective actions, refer to the specific SW-846 method or Method 8000. Note that in a multianalyte method, failure to meet the calibration verification requirement for a small percentage of analytes should not be cause to omit the entire analysis for a sample from regional databases. Omission should be determined on an analyte by analyte basis.

5.7 Analytical Quality Control

Chapter one of SW-846 includes specific recommendations for QC samples, control limits and corrective actions. In choosing an approach to analytical QC, a laboratory should keep in mind that QC sample results help define both method performance and data quality. The appropriate level of QC for a given set of samples is dependent upon the challenges posed by the complexity of the analytical method, the sample matrix and the detection limit requirements of the project. In addition, the end use of the data can determine QC sample type and frequency, calibration requirements, control limits and the corrective actions. The QC required for a project must also account for eventual program driven data qualification. Appendix C to the QA Chapter (PSEP, 1997b) summarizes many of the program specific requirements for QC.

EPA methods (1600 series) that follow the EPA Environmental Methods Management Council's *Format for Method Documentation* (distributed by EPA Environmental Monitoring Management Council, Washington, DC, Nov. 18, 1993) are performance-based and include comprehensive QC procedures and acceptance criteria. These QC procedures provide useful guidance for implementation of new methods.

All quality control data should be maintained and available for easy reference or inspection. Following is a summary of minimum required QC sample types and control limits for organic analysis. A tabular summary of QA/QC frequencies can be found in Table 3 at the end of this section.

Note that this section on analytical QC is not intended to provide criteria that are more lenient or rigorous than the published methods. It should be used to provide guidance when the corresponding level of detail is not available. This section can also be used to guide project planning. It is recommended to use the guidance in the following order:

- use any changes as described in the project planning document,
- use program requirements when available,
- use the method as prescribed.

5.7.1 Method Blanks

Method blanks are analyzed to assess possible laboratory contamination of samples associated with all stages of preparation and analysis of sample extracts. Contamination is of concern because it can result in false positive results (i.e., erroneous reports of the compound as present in the sample) or overestimates of sample concentrations. Alternatively, it is possible that method blanks could incorrectly indicate contamination to be present in a sample. If analyte data are incorrectly rejected on the basis of positive method blank results, then a false negative result would occur. Protection against false positive results is given greatest weight in programs that generate data for possible use in litigation.

5.7.1.1 Frequency

At a minimum, one method blank should be run for every extraction batch (or for volatile compound analyses, every 12 hours or for every analytical instrument sequence, whichever is more frequent).

5.7.1.2 Action Limits

The action limit for a contaminant is reached when its concentration in a blank exceeds the quantification limit.

5.7.1.3 Corrective Action

If action limits are exceeded, analyses should be halted until the contaminant source is eliminated or greatly reduced, or the data recipient has been notified and an acceptable plan of action has been determined.

Laboratories should report original sample data without blank correction and should report data for all method blanks such that the contribution to associated samples can be determined.

The following compounds are some of the common laboratory contaminants that often appear in method blanks: methylene chloride, acetone, toluene, 2-butanone and selected phthalate esters, including bis(2-ethylhexyl) phthalate, butyl benzyl phthalate and di-*n*-octyl phthalate.

5.7.2 Surrogate Spike Compounds

A surrogate is a type of check standard that is added to each sample in a known amount prior to extraction or purging. The surrogate is not one of the target compounds for the analyses, but should have analytical properties similar to those compounds. Because surrogate spikes are the only means of checking method performance on a sample-by-sample basis, they are required for all methods except isotope dilution methods.

5.7.2.1 Compound Type

A minimum of six surrogate standards should be added to each sample (three neutral and three acid compounds) when analyzing for semivolatile organic compounds. These surrogate standards should cover a wide elution range and include one of the more volatile compounds (e.g., d_5-phenol) as well as a degradable PAH [e.g., d_{12}-perylene or d_{12}-benzo(*a*)pyrene]. Three surrogate spikes are required for the analysis of volatile compounds.

Surrogates need not be isotopically labeled. They need only be compounds that are physically and chemically similar to the analytes. Surrogates should be compounds not expected to be present in the samples and should not interfere with target compounds during analysis.

At least one surrogate compound is required as a check on recovery of pesticides and PCB mixtures.

This compound must be well-resolved from other peaks, must not co-elute with any PCB or pesticide analyte and should behave similarly to the analytes. This surrogate will likely not be a perfect PCB/pesticide analog. Possible standards are dibutylchlorendate, hexabromobenzene, decachlorobiphenyl (used by EPA/WDOE Manchester Laboratory and Metro), dibromooctafluorobiphenyl (used by Northwest NMFS and by EPA/WDOE Manchester laboratory) and isodrin (the endo-endo isomer of aldrin), in addition to the compounds cited in SW-846.

5.7.2.2 Frequency

Surrogate spikes should be added to each sample, blank and QC sample, unless the isotope dilution technique is used.

5.7.2.3 Action Limits

The action limits in SW-846 are recommended for use in evaluating surrogate recoveries. Laboratories are encouraged by SW-846 to evaluate the performance of their own method and establish empirical limits. The SW-846 limits are only valid if surrogates are added at the concentrations specified in the methods.

5.7.2.4 Corrective Action

Corrective actions should be outlined in the project plan and should involve consultation with the laboratory. The corrective actions specified in SW-846 should be followed when action limits for surrogate recoveries are exceeded.

Percent recovery values for all surrogate compounds analyzed in sample and method blanks should accompany all data. Data are not to be recovery corrected.

5.7.3 Analytical Replicates

Analytical replicates provide precision information on the actual samples. Replicate analyses are useful in assessing potential sample heterogeneity and matrix effects. In most cases, duplicates are sufficient when using a protocol that is well proven in the laboratory. Replicates may be taken in the field (i.e., multiple samples collected at the same sampling site) or may be a sample that is subsampled by the laboratory to create a repeated analysis. These guidelines are intended to be used for laboratory replicates. Because precision can only be estimated from positive results, the project manager should inform the laboratory which samples to analyze in replicate if there is preliminary information as to which samples are likely to contain measurable levels of the analytes.

5.7.3.1 Frequency

If 1-20 samples are submitted for analysis, at least one laboratory replicate should be analyzed. If more than 20 samples are submitted one replicate should be run for each 20 samples. Note that some programs require analysis of a triplicate measurement. Some programs also allow the matrix spike duplicate to serve as the analytical replicate.

5.7.3.2 Action Limits

Based on data of Horwitz et al. (1980), who charted interlaboratory precision as a function of concentration, a 30 percent coefficient of variation (a statistical measure of precision) is expected for concentrations ranging between 1 and 50 µg/kg dry weight. Extensive discussion of precision requirements occurred at a Puget Sound organics workshop in 1985 and in subsequent work sessions. Based on professional judgment of analysts and regional program managers in attendance, it was decided that a difference of no more than a factor of 2 among replicates would be the basis for the laboratory action limit (i.e., approximately 50 percent coefficient of variation). Exceedance of the action limit would require automatic reanalysis to confirm the results. In the case where results are below the quantification limit, qualification of data may be appropriate for action level exceedances, however, rejection of data may not be appropriate due to the inherent variability of results below the quantification limit. There was discussion about easing the action limit if the results were well beyond some regulatory guideline for acceptable contamination, and tightening the action limit if the results were close to some regulatory guideline. However, most data will have multiple uses and adjustable limits will be difficult to apply as a laboratory control.

5.7.3.3 Corrective Action

If results fall outside the action limit for more than two compounds, a repeat analysis is required to determine the origin of the problem before any data can be reported. If results continue to exceed action limits, subsequent corrective action is at the discretion of the program manager or project coordinator.

A discussion of the results of duplicate sample analysis should include probable sources of laboratory error and an assessment of natural sample variability. When data are qualified on the basis of duplicate results, rationale for assigning the data qualifier should be provided.

5.7.4 Matrix Spikes

Percent recoveries of matrix spikes are commonly reported by laboratories, and matrix spikes are required by SW-846. Matrix spikes should include a wide range of representative analyte types (preferably all analytes). Compounds should be spiked at about five times the concentration of compounds in the sample or five times the quantification limit.

Note that for several of the major programs in the Puget Sound region, all target analytes must be spiked. The results are subsequently used to qualify associated samples. See Appendix C Table C-2 (frequency of QC) and Table C-3 (data qualification) of the QA Chapter (PSEP, 1997b) for additional guidance.

Spiking concentrations that are low relative to sample concentrations increase random error in the determination of the percent recovery. Anomalous matrix spike recoveries may result from random error in measurement rather than interference or matrix effects, and therefore poor results alone should not be cause for data qualification. Spiking the matrix samples at excessively high concentrations may reduce their value for elucidating the effects of the matrix on the pollutants that may be present in the sample.

For comparison, Method 8270 spiking levels for sediments result in approximately 100 ng on-column for organic base/neutral compounds and 200 ng on-column for organic acids, assuming a one-mL final dilution volume, 100 percent recovery and undetected concentrations in the unspiked sample. These levels represent approximately 6,700-13,000 µg/kg dry weight assuming a 30-gram sediment sample with 50 percent moisture.

The same spiked amount in a 100-gram sample with 50 percent moisture would result in approximately 2,000-4,000 µg/kg dry weight concentrations under the same assumptions for other variables. This

spiking level would be approximately 40-80 times a detection limit of 50 µg/kg dry weight for SW-846 procedures (i.e., assuming lowest calibration at 10 ng on-column and 0.5-mL final dilution volume).

5.7.4.1 Frequency

If fewer than 20 samples are submitted, at least one matrix spike (MS) and one matrix spike duplicate (MSD) should be run. If 20 or more samples are submitted, one matrix spike and one matrix spike duplicate should be run for each 20 samples. Note that some programs allow an MS/MSD pair to be used as a sample replicate.

5.7.4.2 Action Limits

Recovery of greater than 50 percent and less than 150 percent of matrix spike compounds accompanied by good precision (RSD less than 50 percent) is considered to be acceptable. Low matrix spike recoveries may result from matrix interferences in the sample. The high component of random error in the recovery value makes it a poor indicator of bias. Therefore, poor results alone should not be cause for data qualification. Rigorous control limits for qualifying data are not recommended because of the potential difficulty in determining when matrix spike results indicate bias due to sample interferences rather than the expected random error of the difference between sample results before and after spiking

5.7.4.3 Corrective Action

In the event of poor matrix spike performance, alternative QA measures should be considered before any associated sample data are qualified as estimates or underestimates, or in very extreme cases, rejected. These measures include results of reference material analyses, surrogate recoveries and the physical percent recoveries of internal standards. Professional judgment must be used to determine which samples should be associated with each matrix spike analysis. An explanation of low percent recovery values for matrix spike results should be discussed in the case narrative accompanying the data package.

Concentrations of compounds in contaminated urban bay samples often exceed reference area concentrations by 10-100 times, and they may even exceed the upper calibration range of the method. Ideally, matrix spike results would be obtained for a range of sample types, from reference sediment to highly contaminated samples. Given limited resources, it is probably of greater value to assess possible interferences in moderately contaminated samples than in reference area samples.

5.7.5 Spiked Method Blanks

Spiked method blanks (SMBs), sometimes called check standards or laboratory control samples (LCS), are method blanks spiked with surrogate compounds and analytes. Such samples are useful in verifying acceptable method performance prior to and during routine analysis of samples. Spiked method blanks do not take into account sample matrix effects, but can be used to identify basic problems in procedural steps. Spiked method blanks can also provide minimum recovery data when no suitable RM is available or when insufficient sample size exists for matrix spikes. Target analyte compounds and surrogate compounds should be added to a method blank prior to extraction. SMBs should be spiked at the same level as the matrix spike.

5.7.5.1 Frequency

If fewer than 20 samples are submitted, at least one spiked method blank should be run. If 20 or more samples are submitted, one spiked method blank should be run for each 20 samples.

5.7.5.2 Action Limits

The action limits used for matrix spikes in the same set of data are recommended for use in evaluating spiked method blank recoveries. If possible, action limits can be developed from historical data by the laboratory.

5.7.5.3 Corrective Action

Spiked Method Blanks are not currently used to qualify data for Puget Sound programs. However, they provide valuable method performance information. In instances where an SMB exceeds control limits for multiple compounds, and other QC sample information indicates that the method has also not performed for samples, corrective action (including reextraction of associated samples) is recommended.

Data should be reported for blank spike analyses in the same manner as matrix spike results.

5.7.6 Reference Materials

The following definitions of reference materials will be adhered to throughout these guidelines:

- Reference Material (RM)—A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.
- Certified Reference Material (CRM)—A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body (e.g., National Research Council of Canada, National Institute of Standards and Technology). A standard reference material (SRM) is a CRM issued by the National Institute for Standards and Technology.

A list of vendors and suppliers of reference materials can be found in Appendix C in this chapter.

RM and CRM provide information on the accuracy (i.e., how near the measurement is to its true value) as opposed to precision (i.e., how near replicate measurements are to each other). When analyzed in replicate, RM and CRM provide information on both accuracy and precision for a particular matrix type. Routine analysis of the regional reference material (RRM) for Puget Sound sediment is recommended to provide data for interlaboratory comparisons.

5.7.6.1 Frequency

If five or fewer samples are submitted for analysis, one RM (or CRM, if available) is recommended, at the discretion of the project coordinator. If analysis of an available reference material is not included, the data may be qualified before entry in regional databases. If 6-50 samples are submitted, at least one RM should be analyzed. For submittals of more than 50 samples, one RM should be analyzed for each 50 samples.

5.7.6.2 Action Limits

Action limits are only appropriate for analysis of CRM (i.e., action limits are not recommended for RM analyses). Follow the limits specified from the supplier of the CRM, where possible. If CRM are unavailable, control limits may not be appropriate, but analyses of RM can still be used to assess overall accuracy or method bias (in conjunction with matrix spikes and surrogate compounds).

5.7.6.3 Corrective Action

It is recommended that the CRM, if available, be analyzed prior to analysis of any samples. If values are outside the action limits, the CRM should be reanalyzed to confirm the results. If the values are still outside action limits in the repeat analysis, the samples may be analyzed and reported with statements that describe the possible bias of the results in the cover letter accompanying the data. Alternatively, the laboratory may be required to repeat the analyses until action limits are met before continuing with sample analyses. Determination of the appropriate corrective action is the responsibility of the program manager or project coordinator and should be specified in the project planning document.

The laboratory should keep a running record of results obtained for each analysis of a CRM. Observed results should be compared to the mean provided by the originator of the CRM, the observed mean obtained from repeated analyses by the laboratory and acceptable range limits. Minimum reporting of RM results with laboratory data should include observed and expected values and the acceptable range limits. The steps for corrective action and observed bias relative to existing CRM values should be reported and discussed in the cover letter.

5.7.7 Control Limits

Control limits for analytical QC samples are described above. Project planning documents may specify control limits that are different from these, when appropriate, and project managers must develop project specific control limits in consultation with the laboratory. For example, a program may require laboratory results for an analyte that is not routinely measured and best available technology for that analyte may not be well demonstrated or documented.

5.7.8 Corrective Actions

The analyst is responsible for monitoring the analysis and troubleshooting problems as they occur. It is important to identify potential analytical problems as soon as possible so that corrective actions can be taken prior to the expiration of holding times. It is the responsibility of the laboratory to communicate analytical problems to the project manager during the analysis so that the project manager may have input into the course of corrective action. This communication is important when the laboratory is experiencing difficulty in meeting any project specific requirements, including detection limits. When reasonable corrective actions do not bring QC sample results into control, resulting data may need to be qualified, depending upon specific project requirements as documented in the project planning document. It is important for the laboratory and the project manager to agree on what constitutes reasonable corrective actions, acceptable data and the appropriate circumstances for data qualification.

TABLE 3
SUMMARY OF QUALITY CONTROL SAMPLES

Analysis Type[1]	Recommended Minimum Frequency of Analysis[2]
Surrogate spikes	Required in every sample and QC: Semivolatiles: 3 for neutral fraction + 3 for acid fraction Volatiles: 3 Pesticide/PCB: 1 preferably 2
Method blank	Semivolatiles: one per extraction batch Volatiles: one per extraction batch or one per 12-hour shift, whichever is more frequent
Reference materials[a]	≤50 Samples: one per set of samples submitted to laboratory >50 Samples: one per 50 samples analyzed
Replicate analyses[b]	≤20 Samples: one duplicate per set of samples submitted to the laboratory >20 Samples: 5 percent of total number of samples
Matrix spikes	≤20 Samples: two per set of samples submitted to laboratory >20 Samples: additional MS/MSD pair for a minimum of 10% spikes
Spiked method blanks	≤20 Samples: one per set of samples submitted to laboratory >20 Samples: additional spike for a minimum of 5% spikes
Field replicates	At the discretion of the project coordinator
Field Blanks	At the discretion of the project coordinator

Notes:

1. The definition of each type of quality control sample is given in the Section 5.7 of this chapter.
2. Some programs may require higher levels of effort. See Section 5.7 of this chapter for full descriptions of recommended frequencies.

a. As available, see Appendix C of this chapter. If available, certified reference materials should be used.

b. Some programs allow the matrix spike duplicate to serve as the analytical replicate.

6. REPORTING AND DELIVERABLES

Specific deliverable requirements must be outlined in the project planning document. Care must be taken to ensure that deliverable requirements meet project data use goals. At a minimum, the laboratory should provide a data report that includes analytical results, a tabular summary of associated QC results and control ranges, and a cover letter that references or describes the analytical procedure(s) and discusses any analytical problems. The following sections describe recommended deliverables to be included in laboratory reports.

6.1 Recommended Deliverables for Organic Analyses

- Date of extraction and analysis;
- Tabulated sample results with units, including reporting basis (e.g. wet, dry, TOC normalized);
- Summary of extraction procedure;
- Detection limits, including both quantification limits and statistically derived detection limits;
- Quantification of all analytes in method blanks and association of method blanks with each sample;
- Tentatively identified compounds (if requested) and methods of quantification;
- Summary of results and control limits for all QC analyses performed by the laboratory, such as spikes, surrogates, duplicates and CRMs;
- Explanations for all data qualifications;
- Reference method and
- Explanations for all departures from the analytical protocols and discussion of possible effects on the data.

6.2 Backup Documentation

All laboratories are required to submit results that are supported by sufficient backup documentation, maintained at the laboratory, and quality control results to enable independent QA reviewers to evaluate data quality and reconstruct final results from the raw data. Legible photocopies of original data sheets should be available from the laboratory with sufficient information to unequivocally identify the following items:

- calibration results;
- method blanks;
- samples, sample sizes and dilution factors;
- replicates and spikes, including amount spiked;
- control or reference samples;
- chromatograms;
- GC/MS tuning documentation;
- GC/MS supporting spectra;
- chain of custody and sampling records and
- any anomalies in instrument performance or unusual instrument adjustments.

7. GLOSSARY

Accuracy - The agreement between an analytical result and the true value.

Action Limit - In Puget Sound programs, a value for results of a QC analysis for which data returned by a laboratory are subjected to qualification before inclusion in a regional database. Also, data obtained when a system or method is not in control may be omitted from a regional database. Note that in a multianalyte method, failure to meet the calibration requirement for a small percentage of analytes should not be cause to omit the entire analysis for a sample from the database. Omission should be determined on an analyte by analyte basis. Action limits and appropriate corrective actions are specified contractually.

Analyte - That which is analyzed.

Assessment - The evaluation process used to measure the performance or compliance of sampling and analysis activities.

Audit - A systematic and independent examination to determine whether sampling and analysis activities and related results comply with planned practices, whether these practices are implemented effectively, and whether the nature and extent of these practices are suitable for the sampling and analysis activities they support.

Batch - The number of samples that are prepared or analyzed with associated laboratory QC samples at one time. A typical batch size is 20 samples and may be dependent on the method.

Bias - The systematic or persistent distortion of a measurement process which causes errors in one direction.

Blank-corrected Result - Refers to an analytical result that has been corrected (mathematically or through analytical procedures) for the contribution of the method blank. The method blank should be processed concurrently. Any correction should account mathematically for all relevant weights, volumes, dilutions and other similar sample processing elements.

Calibration - The determination of the relationship between analytical response and concentration (or mass) of the analyte.

Certified Reference Material - A reference material accompanied by, or traceable to, a certificate stating the concentration of chemicals contained in the material. The certificate is issued by an organization, public or private, that routinely certifies such material (e.g., National Institute of Standards and Technology, American Society for Testing and Materials).

Chain of Custody - An unbroken trail of accountability that ensures the physical security of samples, data and records.

Check Standard - A QC sample prepared independently of calibration standards, analyzed exactly like the samples, and used to estimate analytical precision and indicate bias due to calibration.

Coefficient of Variation - The standard deviation expressed as a percentage of the mean. Also termed relative standard deviation or RSD.

Comparability - An indication of the confidence with which one data set can be compared to another.

Completeness - A measure of the amount of valid data obtained from sampling and analysis activities compared to the amount that was expected to be obtained.

Control Limit(s) - A value or range of values against which results of QC sample analyses are compared in order to determine whether the performance of a system or method is acceptable. Control limits are typically statistically derived. When QC results exceed established control limits, appropriate corrective action should be taken to adjust the performance of the system or method.

Corrective Action - Measures taken to remove, adjust, remedy or counteract a malfunction or error so that a standard or required condition is subsequently met.

Data Quality Objectives - Data quality objectives are qualitative and quantitative statements that define the appropriate type and quality of data needed to support the objective of a given project.

Duplicate Analysis - Analysis performed on a second subsample in the same manner as the initial analysis, used to provide an indication of measurement precision.

Elutriate - A standard test used to predict the release of contaminants in sediment to a water column resulting from open water disposal of the sediment.

Field Blank - A simulated sample (usually consisting of laboratory pure water) that is taken through all phases of sample collection and analysis. Results of field blank analyses are used to assess the positive contribution from sample collection and analysis procedures to the final result.

Guideline - A suggested practice that is non-mandatory.

Isotope Dilution Technique - An internal standard technique for quantification of organic compounds that uses a large number of stable isotopically labeled compounds spiked into the sample before extraction to provide recovery correction (i.e., to correct for compound loss during sample workup on a sample-specific basis). The labeled compounds are analogs of the target compounds and are assumed to behave similarly. The isotopic labels typically involve replacement of hydrogen atoms with deuterium or replacement of carbon-12 atoms with carbon-13 atoms.

Matrix - The sample material in which the analytes of interest are found (e.g., water, sediment, tissue).

Matrix Spike - A QC sample created by adding known amounts of analytes of interest to an actual sample, usually prior to extraction or digestion. The matrix spike is analyzed using the normal analytical procedures. The result is then corrected for the analyte concentration determined in the unspiked sample and expressed as a percent recovery. This provides an indication of the sample matrix effect on the recovery of target analytes.

Method - A body of procedures and techniques for performing an activity that is systematically presented in the order in which they are to be executed.

Method Blank - A QC sample intended to determine the response at zero concentration of analyte. A

clean matrix (generally water) known to be free of target analytes that is processed through the analytical procedure in the same manner as associated samples.

Method Detection Limit - The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing the analyte.

Metro - King County Water Pollution Control Division Environmental Laboratory.

Must - A requirement that has to be met.

Normalize - Perform a data calculation in order to express results in terms of a reference parameter or characteristic.

Precision - The statistical agreement among independent measurements determined from repeated applications of a method under specified conditions. Usually expressed as RPD, RSD or coefficient of variation.

Project - An organized set of activities within a program.

Quality Assurance - An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item or service is of the type and quality needed and expected by the customer.

Quality Control - The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process. Quality Control is an element of quality assurance. Analyses of QC samples and auditing/assessment are common quality control activities.

Qualified Data - Data to which data qualifiers have been assigned. Data qualifiers provide an indication that a performance specification in the qualified sample or an associated QC sample was not met.

Quality Assurance Project Plan - A formal planning document describing in comprehensive detail the necessary QA, QC and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

Quantification - The process of calculating the value of an analyte in a particular sample.

Recovery - The percentage difference between two measurements, before and after spiking, relative to the concentration spiked.

Replicate - One of several identical experiments, procedures or samples.

Reproducibility - The ability to produce the same results for a measurement. Often measured by determining the RPD, RSD or coefficient of variation for an analysis.

Representativeness - A measure of the degree to which data accurately and precisely represent an environmental characteristic or condition.

Reference Material - A material of known analyte composition which can be used for comparison of analytical results. The reported analyte concentrations have not been certified (see Certified Reference Material).

Relative Percent Difference - Difference of two measurements x_1 and x_2, divided by the mean of the measurements, multiplied by 100.

Percent RSD - Calculated by dividing the standard deviation by the mean and multiplying by 100.

Relative Standard Deviation - see coefficient of Variation.

Semivolatile Organic Compounds - Gas chromatographable organic compounds with moderate or low vapor pressures that can be extracted from samples using organic solvents.

Should - Refers to a highly recommended practice. The practice may be mandatory, depending on the exact conditions of data generation.

Spike - The addition of a known amount of a substance to a sample or a blank.

Spiked Method Blank - See Check Standard.

Standard - A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of a sample. In chemical measurements, standard often describes a solution of analytes used to calibrate an instrument.

Standard Reference Material - A material with known properties produced and distributed by the U. S. National Institute of Standards and Technology (NIST).

Surrogate Spike Compound - A compound that has characteristics similar to that of a compound of interest, is not expected to be found in environmental samples, and is added to a sample prior to extraction. The surrogate compound can be used to estimate the recovery of chemicals in the sample.

Target Analytes (or Target Compounds) - One or more elements or compounds which are intended to be determined by an analytical procedure (in contrast to tentatively identified compounds).

Tentatively Identified Compounds - Chemicals identified in a sample on the basis of mass spectral characteristics held in common with a reference mass spectra of a known chemical. These compounds cannot be more confidently identified unless a reliable standard of the compound is obtained and is confirmed to co-elute with the tentatively identified compound and generate similar mass spectra using the same GC/MS.

Validation - Confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Can refer to a process whereby environmental data are determined by an independent entity to be complete and final (i.e., subject to no further change), and to have their value for the intended use described by both qualitative and quantitative statements.

Volatile Organic Compounds - Organic compounds with high vapor pressures that tend to evaporate

readily from a sample.

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9. APPENDIX A -- RECOMMENDED METHODS FOR ORGANOTIN COMPOUNDS

At a workshop conducted in June, 1995 laboratory representatives indicated that the organotin methods cited in the previous releases of PSEP had been used successfully on many projects. The overall agreement was to leave the recommended method as written, however, some changes have been made to reflect on going method improvements.

The following summary is from the workshop of the Subcommittee on Organotin Analysis Methods held on 25 September 1987 at EPA Region 10, Seattle, WA. The purpose of the workshop was to provide input on appropriate analytical methods and to reach some consensus on appropriate methods of analysis for organotin species (i.e., tetrabutyltin, tributyltin, or TBT, dibutyltin and monobutyltin) present in water, sediment and tissue samples. The discussions were based on information published by Matthias et al. (1986a,b), National Bureau of Standards (NBS) (1986), Muller (1987) and Rice et al. (1987) and based on work completed by participants in the workshop. Recommendations are summarized below. A similar method is described in Krone et al. (1989), revised March 1995.

9.1 Sample Containers and Handling

For water samples, the use of either polycarbonate or borosilicate glass containers with polytetrafluoroethylene (PTFE) (e.g., Teflon®) lined lids was recommended. Losses of organotin species were reported when other container materials were used (NBS 1986). For sediment or tissue samples, soft, flint glass jars with PTFE-lined lids appear to be adequate. It was recommended that all samples (i.e., tissue and sediment) be frozen within 24 hours of collection to prevent any possible degradation of tin compounds. It is recommended that unfrozen samples be extracted and derivitized within 14 days to minimize the possibility of hydrolysis or degradation of butyltin compounds. Sample holding times prior to extraction or analysis were not discussed, but analysis should be completed as soon as possible to prevent potential degradation of the sample.

9.2 Surrogate and Internal Standards

The use of a surrogate standard to check analyte recovery was an important issue. A surrogate standard is defined as a compound that is added to the sample at the beginning of the extraction procedure to estimate potential loss of analyte during sample preparation and analysis. The primary surrogate standard recommended was tripropyltin chloride, which is available from Alfa Products, Danvers, MA or from Aldrich.

Other researchers are using tripentyltin chloride as a surrogate standard. Tripentyltin was adopted as a secondary surrogate standard.

In all cases, the primary surrogate should be used as a minimum to check on analyte recovery. If the secondary surrogate is available, it may also be used.

The use of an internal standard was also discussed. An internal standard is defined as an analyte that is added to the sample extract just prior to injection of the sample into an instrument (e.g., gas chromatograph). The internal standard should be fully substituted and not require derivatization prior to analysis. Tetrapentyltin was recommended as a possible candidate for use as an internal standard and is available from Aldrich. Tripentylmonobutyltin can be successfully used as a GC internal standard (Krone et al., in press).

9.3 Detection Limits and Data Reporting

Because regulatory action levels have not been established for butyltin compounds, the following detection limits (as TBT) were agreed upon as guideline levels:

Water	1 ng/L
Sediment	10 µg/kg dry weight
Tissue	50 µg/kg wet weight

These concentrations were chosen because of the potential for toxic effects at low concentrations of butyltin compounds.

It is recommended that results be reported as µg TBT/kg sample rather than in units of tin. This is recommended because TBT is reported in units of TBT in both EPA's Ambient Aquatic Life Water Quality Criteria for TBT (March 1991) and the Superfund Program's sediment and water screening criteria for TBT (under preparation).
Analytical interference by sulfur species should be reported.
To convert TBT data reported on a different basis, the following conversions can be made:

TBT reported as	Convert to	Conversion factor
µg Tin/kg	µg TBT/kg	2.44
µg TBTCl/kg	µg TBT/kg	0.89
µg TBTO/kg	µg TBT/kg	0.95

Similar conversions should be made for all reported species.

9.4 Quality Assurance

For any laboratory conducting butyltin analysis, an initial method performance evaluation should be performed for each matrix analyzed. This procedure would be similar to that required by EPA 600 series methods for analysis of organic compounds. For an example of the method performance evaluation procedures, see Section 8 of EPA Method 625 (EPA, 1982).

Method blanks and spike recoveries should be reported with each sample set. Five to ten percent of all samples should be spiked, in duplicate, to determine analytical recoveries and assess precision. Data should be reported without any blank correction or other adjustments.

The NBS research material, "Tributyltin in Water," could be run as an external check on laboratory capabilities.

9.5 Extraction Procedures

9.5.1 Water

The most efficient and tested method of analysis for water appears to be a method developed by Matthias et al. (1986a,b). This method involves in situ reaction of organotin compounds with sodium borohydride and simultaneous extraction of the water sample with methylene chloride. Detection limits of 7 ng/L have been reported for a 100-mL sample volume. Lower detection limits can be achieved using larger sample volumes. The Matthias et al. (1986a,b) procedure has been adopted in Great Britain as an official method.

9.5.2 Sediment

The committee agreed there are still problems with methods involving the formation of hydride derivatives of organotin compounds in sediment and tissue. The group debated whether Soxhlet extraction procedures could effectively remove all organotin compounds present in a sample and concluded that tropolone was needed as a complexing agent to efficiently extract the organotin compounds from complex matrices. However, because tropolone will not cycle in a Soxhlet extraction apparatus, use of this apparatus is not recommended. It has also been found that the addition of activated copper, as described in Sloan et al. (1993), can decrease the interferences from sulfur that are discussed in Section 9.6.

Drying of the sample matrix is not recommended prior to extraction. The committee agreed that the best way to dry samples is with anhydrous sodium sulfate after acidifying the samples to pH 2 using HCl. Drying with sodium sulfate is simultaneous with extraction with a mixture of tropolone and methylene chloride. Overnight extraction is conducted by shaking or tumbling.

After extraction, the solvent is concentrated and exchanged to an appropriate solvent for a Grignard reaction. The hexyl Grignard derivatives of the organotin compounds are then formed. This step is followed by a column cleanup procedure using either silica gel or Florisil®.

The publications of Muller (1987) and Krone et al. (1989) may be consulted for detailed procedures that meet the criteria outlined above for the analysis of organotin compounds in sediment.

9.5.3 Tissue

Tissue samples can be extracted using a procedure similar to the one for sediments. However, the tissue sample should be ground using a homogenizer with the tropolone/methylene chloride extraction solvent. Anhydrous sodium sulfate should be added to dry the sample during the extraction. After concentration and exchange of the solvent, the hexyl Grignard derivatives are formed. This step is followed by column cleanup using either silica gel or Florisil®. Additional details are included in Krone et al. (1989).

9.6 Instrumentation

Use of gas chromatography/flame photometric detection (GC/FPD), gas chromatography/mass spectrometry (GC/MS) and gas chromatography/atomic absorption spectroscopy (GC/AA) were agreed upon for the final determination of butyltin compounds. Details on the use of each method are summarized below. Laboratories have also successfully employed the use of GC/MS SIM and GC/AED for the analysis of organotins.

Because of possible interference by sulfur species, the use of dual channel GC/FPD is recommended. A 600-2,000 nm band pass filter is needed in the channel used for determination of butyltin species. Sulfur determination is conducted at 393 nm in the second channel (Matthias et al., 1986a,b). If peaks occur at the same retention time in both channels, dual column confirmation of butyltin compounds using polar and semipolar columns is required. Otherwise no further actions are necessary. Because of the potential complexity of samples and unknown interferences, GC/MS should be used for confirmation of the butyltin species until additional data can be acquired on potential interferences. As more data are generated in the future, the use of dual channel GC/FPD may prove to be sufficiently reliable such that GC/MS confirmation of organotin compounds might only be needed for analyses conducted on complex matrices.

The use of GC/AA also requires dual column confirmation as stated above for GC/FPD. The tin absorption signal is monitored by the AA. Committee members noted that some groups took 6 months to overcome problems associated with the hybrid GC/AA system. Discussions with researchers who have developed GC/AA systems may shorten start-up times. As above, GC/MS should be used for confirmation of butyltin compounds determined by this instrument combination until additional data can be acquired on potential interferences.

GC/MS was recommended as an analytical instrument for use, as long as the detection limits specified above can be obtained. The data obtained by GC/MS do not require confirmation by another instrumental method.

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10. APPENDIX B-GUIDANCE FOR SELECTED ION MONITORING

10.1 General Comments

Selected Ion Monitoring (SIM) analysis is accepted as a method for detection and quantification of low concentrations of organic compounds. It has been applied to waters, soil, sediments and tissue samples. There are no "official" methods for this technique available for reference. The technique can be done on most commercially available GC/MS systems. Laboratories using this technique have adapted existing written methods to accommodate the use of SIM.

The lack of an official method means that there are method and procedural differences between individual laboratories. If SIM is to be used to produce data for the Sediment, Water and Tissue efforts in the Puget Sound region, then a set of consistent conditions must exist between the various generators of SIM data. The sections below are several areas in which the methods must have some consistency. The comments within each section are derived from review of several working Standard Operating Procedures (SOPs) provided for review by participating laboratories and the notes from a recent workshop on the SIM technique. The SOPs, in general, were patterned after SW-846, method 8270 (most recent edition). The SIM procedures are primarily used to analyze and quantitate polynuclear aromatic hydrocarbons (PAH), phenols and phthalates. SIM may be used for PCB analysis; however, the vast majority of PCB analysis is done on GC/ECD.

10.2 Tuning

Two major tuning techniques are used in SIM methods. One technique uses the existing compound DFTPP and its associated EPA criteria for setting and maintaining tune. The other technique use the standard MS tuning compound, PFTBA (also know as FC-43) adjusted to the normal default mass abundance criteria. One SOP used modified mass abundance criteria for PFTBA to maximize sensitivity for masses below 350 amu. Whichever technique is used, it must be consistently applied throughout the analysis of samples for a project.

The use of the DFTPP tuning criteria is recommended for consistency.

10.3 Calibration

Calibration curves of three, five, six and seven points have been used. Recommended on-column amounts should be in the range of 0.02 to 2 ng. A wide calibration range (use of five or more points) is recommended due to the high sensitivity of the method. A wider range should allow for analysis of fewer diluted samples as well. If possible, all compounds of interest should be analyzed in one run. This will minimize the effects of tuning changes caused by analyzing the sample several times.

Acceptance criteria for calibration curves and continuing calibration should be consistent with currently accepted practice, preferable SW-846. Initial calibration curves should meet either percent RSD (internal standard technique) or percent difference (external standard technique) criteria. Continuing calibration should meet percent difference criteria.

10.4 Ions and Acquisition Parameters

The ions used for SIM analysis should be selected from full scan spectrums of each compound on the intended analysis instrument. The recommended number of ions is three to five for targets and two for internal standards. Ions should be chosen based on their uniqueness to the compound and the lack of overlapping or interfering compounds. In the case of PCBs, the most abundant ion from each PCB chloro-cluster should be selected. The base ion for each target compound should be used for quantitation and the remaining ions used for confirmation. The reason for selecting more than two ions per target compound is to strike a balance between sensitivity and confirmation.

Acquisition conditions should allow for at least two scans per second. This will allow the collection of enough information to produce good chromatographic peak shape for quantitation. The dwell times should be set to collect an adequate amount of ion information without overwhelming the data system under the recommended scan conditions. Peak width settings appear to have minimal effect on the sensitivity and confirmation ability of the technique.

10.5 Identification

Identification of the target compounds should be similar to the procedures used for full scan analysis. The peak should be within plus or minus 0.06 relative retention time units of the compound from the standard mix. The relative abundance and relative ratios of the ions should be within an acceptable range (20 percent) of the spectrum generated by the standard. Special attention should be given to the evaluation of possible interferences from the matrix. The lack of additional confirmation ions places more emphasis on identification by retention time. Because retention time begins to play a more important role in identification, then other confirmational techniques should be considered if the SIM analysis employs less than two monitored ions, such as chromatography on a column of different polarity.

10.6 Detection/Reporting Limits

The minimum reportable amount is very dependent on how the tuning and calibration is set up for a SIM method. Therefore, the minimum detection or reporting limits will vary from SOP to SOP. Suggested levels for the lowest reporting limit for analysis of all semivolatile compounds in one analytical run are

Water	0.2 - 0.5 µg/L (PAH, Phenol and Phthalates)
Sediment/Tissue	20-50 µg/kg (PAH, Phenols and Phthalates)

Lower reporting limits may be possible if only one class of compounds in being analyzed.

10.7 Preparation

Preparation of the sample should proceed using accepted methods. Nominal volumes and weight for the fractions should be

Water	1000 ml
Sediment	25-30 g
Tissue	10-30 g (depending on lipid content)

Additional cleanups should still be performed on the sample extracts. SIM cannot be used as a substitute for proper and complete preparation of the sample.

10.8 Quality Assurance

All normally applicable QC should be incorporated into SIM SOPs. Initially default SW-846 or other control limits for surrogates, matrix and blank spike and Laboratory Control Samples (LCS) materials should be used as QC for SIM SOPs. Once sufficient data has been accumulated using SIM SOPs, then new control ranges should be established to more properly reflect SIM method performance. An initial assessment of SIM SOP performance should be performed. These initial precision and recovery values should be used, along with other QC samples, to monitor and control SIM method performance.

10.9 References for Appendix B

Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects, 1984-1992, NOAA Technical Memorandum NOS ORCA 71, NOAA, Silver Springs, MD, July 1993

11. APPENDIX C-SUPPLIERS OF REFERENCE MATERIALS

In Puget Sound, a regional reference material (RRM) has been developed for marine sediments by NOAA/NMFS for EPA, NOAA and other agencies and laboratories. The RRM is a fresh-frozen sediment homogenate from Sequim Bay, spiked with selected organic acid and neutral compounds at low concentrations. Available samples of the RRM can be requested from the EPA Region 10 Office of Puget Sound. This RRM has been analyzed in interlaboratory studies using NOAA methods, the results of which have been compared with analyses by various investigators using different methods. Although not certified, this RRM is useful for intercomparing Puget Sound studies and is strongly recommended in every project.

There is no marine sediment CRM available for organic compounds of concern in Puget Sound from the Puget Sound region, except for a marine sediment certified by the National Research Council (Canada) for organotin compounds (i.e., PACS-1). Tissue homogenates are sometimes available as reference materials (e.g., mega mussel sample, EPA, Environmental Research Laboratory, Narragansett, Rhode Island). An oyster CRM may be available by special request for selected organic contaminants. NRCC supplies CARP-1, which is a ground whole fish slurry CRM for Dioxins, Furans and selected PCB congeners and Cambridge Isotope Laboratories supplies three different ground whole fish slurry RM (as "clean," "contaminated" and "fortified") that have round-robin consensus values.

ORGANIC ANALYSIS AND CRM

CRM Number	Source	Name	Matrix	Preparation
1939	NIST	PCBs in River Sediment.	River Sediment	Total
1941a	NIST	Organics in Marine Sediment.	Marine Sediment	Total
CS-1	NRCC	PCBs	Coastal Sediment	Total
HS-1[a]	NRCC	PCBs	Harbour Sediment.	Total
HS-2[a]	NRCC	PCBs	Harbour Sediment	Total
HS-3	NRCC	PAHs	Harbour Sediment	Total
HS-4	NRCC	PAHs	Harbour Sediment	Total
HS-5	NRCC	PAHs	Harbour Sediment	Total
HS-6	NRCC	PAHs	Harbour Sediment	Total
SES-1	NRCC	PAHs	Estuarine Sediment	Total/Leach
1588	NIST	Organics in Cod Liver Oil	Cod Liver Oil	Total
1974a	NIST	Organics in Mussel Tissue	Tissue	Total

[a] Both SRMs contain Aroclor 1260 in addition to the certified Aroclor 1254 value. These materials also contain substantial amounts of elemental sulfur.

Please note that many of the certified values for the CRM listed in the table was generated using nonstandard extraction techniques. This means that the certified values may not be directly comparable with extraction techniques used in most laboratories. This must be kept in mind when using this information to qualify or validate the generation of sediment, tissue and water data.

SRM and CRM Vendors

National Institute of Standards and Technology (NIST)
Standard Reference Materials Program
Room 204, Building 202

Gaithersburg, MD 20899-0001
Phone: 301-975-6776
Fax: 301-948-3730
e-mail: SRMINFO@enh.nist.gov

This vendor can provide all types of SRMs, including marine tissue, sediment and water (no seawater).

National Research Council of Canada (NRCC)
Institute for Marine Biosciences
Halifax, Nova Scotia, Canada B3H 3Z1
Phone: 902-426-8280
Fax: 902-426-9413
e-mail: crm@imb.lan.nrc.ca

This vendor provides mostly marine materials. These would include sediments and tissue materials.

Resource Technology Corporation
P. O. Box 1346
2931 Soldier springs Road
Laramie, WY 82070
Phone: 307-742-5452
Fax: 307-745-7936

This vendor is both a producer and distributor of CRM and SRM materials. They handle materials from the USA and from European countries as well. They can also prepare a special list of materials on request.

12. APPENDIX D-ORGANIC CARBON NORMALIZATION OF SEDIMENT DATA[1]

12.1 Introduction

All sediment data collected in Washington State are evaluated using the Sediment Management Standards (SMS), Chapter 173-204 WAC. Under the SMS rule, the numerical sediment standards for most organic chemicals are organic carbon normalized. Consequently, all sediment samples that are analyzed for organic chemicals must also be analyzed for organic carbon to facilitate comparisons with the numerical standards.

This technical information memorandum describes why some sediment data are organic carbon normalized, how organic carbon data are collected and analyzed, provides an equation for organic carbon normalization data and explains how to evaluate historical data for which organic carbon data are not available. Finally, guidelines are presented for determining when it may not be appropriate to organic carbon normalize data.

For questions on the enclosed information or for further information, please contact the Sediment Management Unit at 360-459-6824, or contact the NWRO or SWRO Sediment Technical Specialist.

12.2 Why Sediment Data are Organic-Carbon Normalized

Concentrations of organic contaminants (particularly nonpolar, nonionizable chemicals) and the toxicity of these contaminants in sediments have been observed to correlate well with the organic carbon content of sediments (DiToro et al., 1991; Lynman, 1982; Roy and Griffin, 1985). Nonpolar contaminants in sediments or water preferentially partition into the organic material in sediments because of the similar chemical nature of the organic material to the nonpolar organic contaminants. Contaminants that form ions, such as acids, bases, phenols and metals, do not partition as strongly into the organic fraction in sediments.

DiToro et al. (1991) and others have reported that the toxicity of nonionic organic chemicals in sediments appears to be correlated to the concentration of those chemicals in the organic carbon fraction of sediments, but is not well-correlated with the overall (dry weight) concentration of the chemicals in sediments. Therefore, the concentrations of contaminants in the organic fraction of sediments may be more relevant than dry weight concentrations for setting standards that are intended to prevent adverse biological effects.

In addition, because nonpolar organic contaminants are primarily associated with the organic matter in sediments, these contaminants move in the environment along with the organic fraction in sediments and may also move along with suspended organic matter in water. Therefore, gradients of chemical concentration associated with a source may be more easily observed when the data are OC-normalized

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[1] **THIS APPENDIX IS A REPRINT OF A TECHNICAL INFORMATION MEMORANDUM WRITTEN BY TERESA C. MICHELSEN, PH.D. IN DECEMBER 1992, WASHINGTON DEPARTMENT OF ECOLOGY, SEDIMENT MANAGEMENT UNIT.**
MODIFICATIONS ARE FROM A CLARIFICATION PAPER, WRITTEN BY KATHRYN BRAGDON-COOK, WASHINGTON DEPARTMENT OF ECOLOGY, SEDIMENT MANAGEMENT UNIT.

than when they are presented in dry weight.

The Sediment Management Standards criteria for nonionizable organic chemicals have been set on an OC-normalized basis. Because the bioavailability of acids, bases, other ionizable organic chemicals and metals are generally not controlled by organic matter in sediments, standards for these contaminants are set on a dry weight basis.

12.3 Collecting and Analyzing Organic Carbon Data

The organic carbon content of sediments is measured and referred to as *total organic carbon* (TOC). TOC refers to the total amount of organic carbon in the sediment and does not include mineralized carbon present as carbonates or bicarbonates. These inorganic forms of carbon do not substantially affect the partitioning of organic chemicals and are removed from the sample by the laboratory.

TOC samples may be collected in glass or plastic containers. A minimum sample size of 25 grams (wet weight) is recommended. Because a special bottle is not required, sediments for TOC analysis may be combined with sediments for other analyses that will be performed at the same laboratory. Samples should be stored frozen and can be held for up to six months if frozen.

The Department of Ecology Manchester Environmental Laboratory recommends Method 5310B for measuring TOC in wastewater or, with some modification, in sediments. Test Methods for Evaluating Solid Waste (EPA 1995) SW-846 Method 9060 also references *Standard Methods for the Examination of Water and Wastewater* for measuring TOC levels of solid and hazardous waste.

These methods require some modification for measuring TOC in sediment. Standard method 5310B calls for the sample to be treated with HCl to convert inorganic carbon to CO_2 which is then purged using purified gas. The sample is homogenized and diluted as necessary. A portion is injected with a blunt-tipped syringe into a heated reaction chamber (packed with a catalyst) of a carbon analyzer using infrared detection. Needle size is selected to be consistent with particle size. Some accredited laboratories have adapted this technique to sediment by drying the sample at 70 degrees C and using an instrument attachment to the carbon analyzer designed specifically for sediment samples (Dohrman sludge/sediment boat sampler attachment, Model 183, for use with the Dohrman DC-80 TOX analyzer). The sample is then combusted and organic carbon in the sediment converted to CO_2 and transported in carrier gas streams to be measure by an infrared detector.

The carbon analyzer/infrared detection used in these methods identifies characteristic spectral fingerprints as light in the infrared spectrum passes through various molecules. This instrument offers greater sensitivity than the ascarite-filled tube collector (previously referenced in PSEP, 1989) for measuring low levels of CO_2.

Standard Method 5310B and SW-846 Method 9060 provide for sensitive measurement of TOC concentrations in sediment. SW-846 Method 9060 can detect TOC in sediments below 0.1%. For these reasons, utilization of Method 5310B or SW-846 Method 9060 using infrared detection is strongly recommended.

To correct for true dry weight with either method, the corresponding total solids analysis should be run twice, once at 70 degrees C and once at 104 degrees C. and the TOC calculation based on dry weight at 104 degrees C.

12.4 Organic Carbon Normalization of Dry Weight Data

As discussed in Section 12.5, organic carbon (OC) normalization is performed on a sample-by-sample basis, because TOC values vary from station to station. Because some site-specific evaluation is required (see Section 12.7), OC normalization should be performed by the project manager or consultant who receives data from the laboratory. Laboratories are generally not expected to perform the normalization.

To convert chemical concentration data expressed as mg/kg dry weight to mg/kg OC, divide the dry weight concentration by the percent TOC (expressed as a decimal), as shown in the following equation:

$$\text{mg/kg OC} = \frac{\text{mg/kg dry weight}}{\text{kg TOC/kg dry weight}}$$

where: mg/kg OC = milligrams of the chemical per kilogram of organic carbon

mg/kg dry weight = milligrams of the chemical per kilogram of dry weight sample

kg TOC/kg dry weight = percent total organic carbon in dry weight sample (expressed as a decimal; for example, 1% TOC = 0.01)

Although data are typically reported in mg/kg, data reported in µg/kg, ppb, or ppm can also be used in the above equation. For example:

$$\frac{\text{2 ug phenanthrene/kg dry sediment}}{\text{0.01 kg TOC/kg dry sediment}}$$

= 200 ug phenanthrene/kg TOC
= 200 ppb phenanthrene, OC-normalized

Because this conversion is tedious to do by hand for large data sets, the data may either be entered into a spreadsheet or database that can be used to perform the conversion. Contractors providing sediment data for permit applicants, cleanup proponents or for Ecology should perform the normalization (for nonionic organic chemicals) and report the data for these chemicals both as dry weight and as OC-normalized data.

12.5 Typical TOC Values for Sediments

TOC values vary widely in the natural environment. A range of 0.5-3 percent is typical for Puget Sound marine sediments, particularly those in the main basin and in the central portions of urban bays. For example, the Puget Sound Ambient Monitoring Program reports a mean TOC value of 1 percent (PSAMP, 1990). TOC values less than 0.5 percent are commonly found in sandy or gravelly areas, erosional areas or areas with fast-flowing currents (including rivers). In addition, the percent organic carbon in subsurface sediments usually decreases with depth, to as little as 0.01 percent.

Natural TOC values greater than 3 percent are common in nearshore environments. On occasion, natural TOC values of up to 12-15 percent have been observed in Puget Sound and other areas, particularly in depositional and/or quiescent areas where organic matter may collect. Natural TOC values may be much higher in marshy areas or other wetland environments.

TOC values may also be artificially elevated in sediments that are heavily contaminated with organic

substances (sewage, petroleum hydrocarbons, wood chips). Sewage and organic chemicals will typically raise TOC values by at most a few percent; in a majority of the cases, the effect will be negligible. However, organic debris such as wood chips can raise the TOC value by anywhere from several percent to 50 percent or more.

Because TOC values may vary widely within a single site, organic carbon normalization is performed on a station-by-station basis. Therefore, each sample that is analyzed for nonionizable organic contaminants must also be analyzed for TOC.

12.6 Evaluation of Historical Data Sets

Collection of TOC data is currently required for all sediment sampling to allow comparison to numerical sediment standards. However, many historical data sets are not OC-normalized and may not contain station-by-station TOC data. If any TOC data are available for the data set, it is recommended that a conservative value be chosen from the data available that represents the lowest percent TOC observed at the site. If different areas of the site appear to have widely varying levels of TOC, a different value may be chosen for each area that represents the lower end of the range of TOC values for that area. The professional judgment of the site/permit manager should be used to select an appropriate value in each case.

If TOC data were not included in the data set, data may be available from other studies in the same area. The SEDQUAL database may be consulted to determine whether TOC values are available for the area of interest. Again, a value should be chosen that represents the lower end of TOC values for the area, to insure that the OC-normalized concentrations calculated using the general TOC value are protective. If no TOC data are available for the area of interest, the Sediment Management Unit or a regional sediment technical specialist should be consulted to determine an appropriate TOC value to use for the comparison.

12.7 When Organic-Carbon Normalization May not be Appropriate

There are several situations, including those described below, in which it may not be appropriate to OC normalize sediment data. For additional information or guidance on data evaluation and presentation for these situations, contact the Sediment Management Unit or a regional technical specialist. Because of the variety of uses to which sediment data are put, sediment data for nonionic organic chemicals should be reported both as dry weight and as OC-normalized data.

In areas where the TOC is very low or very high, biological testing or use of dry weight concentrations should be considered along with OC-normalized concentrations in evaluating the extent of contamination and potential biological effects.

For example, if TOC values are very low (e.g., 0.5%), it is even possible for background concentrations of organic chemicals to exceed the Sediment Quality Standards when OC-normalized. In this situation, it may be appropriate, on a site-specific basis, to use Apparent Effects Thresholds (AETs) expressed as dry weight (see PSEP, 1988) to evaluate sediment toxicity. Please contact the Sediment Management Unit for assistance in evaluating such data.

Conversely, if TOC concentrations in sediments have been increased above natural concentrations by organic contamination (such as wood chips, sewage or petroleum), the OC-normalized values may be inappropriately low. In these cases, although the OC-normalized chemical criteria would not be

exceeded, the sediments may still cause adverse biological effects and may therefore exceed the narrative standards or biological criteria. To address this concern, if the organic chemical or substances that are the primary contributors to the elevated TOC levels are know, the contribution of the organic contaminants to the percent TOC may be determined through analytical methods and subtracted from the TOC value before OC normalizing. Alternatively, as described above, biological testing or dry weight AETs may be used to evaluate sediment toxicity.

Bulk sediment concentrations expressed as dry weight are used to make decisions regarding treatment and disposal of sediments. Currently, the Puget Sound Dredged Disposal Analysis (PSDDA) program uses dry weight data to determine whether sediments can be disposed of in open-water disposal areas. In addition, upland disposal options require evaluation of whether the sediment exceeds land disposal restrictions and dangerous/hazardous waste thresholds, based on dry weight concentrations. For treatment alternatives, the average dry weight concentrations of chemicals in sediment may be used to predict the effectiveness of processes such as bioremediation or chemical stabilization/solidification.

12.8 References for Appendix D

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